Molecular synthesis in hypervelocity impact plasmas on the primitive Earth and in interstellar clouds

George G. Managadze
Space Research Institute (IKI), Moscow, Russia

William B. Brinckerhoff
Applied Physics Laboratory, The Johns Hopkins University, Laurel, Maryland, USA

Alexander E. Chumikov
Space Research Institute (IKI), Moscow, Russia

Received 9 October 2002; revised 30 November 2002; accepted 17 December 2002; published 13 March 2003.

[1] When impact speeds exceed a critical range of $\sim$15–20 km s^{-1}, the resulting plasma plume energizes very rapidly from a few eV, to as high as 30–50 eV when speeds reach 50–100 km s^{-1}, and can be completely atomized and ionized. During post-impact adiabatic dispersion, the degree of ionization drops. The remaining ion population is mostly atomic, sampling the elemental composition of the colliding bodies, but some molecular ions are also formed. We present here results of experiments in which the physical and chemical conditions in the plume of a hypervelocity micrometeorite impact well above 20 km s^{-1} were modeled with Q-switched laser ablation. The formed molecular ions were analyzed with a time-of-flight (TOF) mass reflectron capable of distinguishing plasma-synthesized from surface-desorbed species. Singly- and multiply-charged small organic molecules were identified as having formed in laser plasmas induced from inorganic carbonaceous substances. The results show the possibility of abiogenic synthesis of organic molecules in hypervelocity impacts of meteors on the primitive Earth during heavy bombardment and of dust particles in interstellar clouds. *INDEX TERMS:* 6022 Planetology: Comets and Small Bodies: Impact phenomena. **Citation:** Managadze, G. G., W. B. Brinckerhoff, and A. E. Chumikov, Molecular synthesis in hypervelocity impact plasmas on the primitive Earth and in interstellar clouds, *Geophys. Res. Lett.*, *30*(5), 1247, doi:10.1029/2002GL016422, 2003.

1. Introduction

[2] Hypervelocity impacts are part of the fundamental dynamics of matter in space, occurring statistically over vast spatial and temporal scales [*Spitzer*, 1978; *Bochkarev*, 1992]. At the multiple-kilometer scale, catastrophic impacts between small bodies and planets in the early solar system strongly influenced the geology and geochemistry of those bodies. During heavy bombardment, 4.5-3.8 Ga, the primitive Earth's surface endured a veritable rain [*Goldsmith and Owen*, 1992] of hypervelocity meteor impacts at fluxes of $\sim 10^3$ J m^{-2} $year^{-1}$ (10^{22} eV m^{-2} $year^{-1}$), comparable to the heat from volcanoes [*Kobayashi and Saito*, 2000]. Velocities ranged from $\sim$10 km s^{-1} to at least 70 km s^{-1}. Near the end of this period, life arose.

[3] In interstellar space and protosolar nebulae, various mechanisms can accelerate $\sim$10–100 nm dust particles to high velocities. For example, the pressure of light or electromagnetic shocks can accelerate dust to well over 100 km s^{-1} [*Bochkarev*, 1992] causing "supercritical" impacts with atomization and ionization fractions approaching unity. Laboratory investigations of impacts are typically carried out in special dust accelerators [*Knabe and Krüger*, 1982; *Ratcliff et al.*, 1997; *Roybal et al.*, 1995], with particles of 10^{-11}–10^{-17} g mass now achieving speeds up to 100 km s^{-1}. Studies with such apparatus are challenging in terms of throughput and expense, and are somewhat limited in scale and compatibility with real-time composition measurements. "Full-scale" in-space experiments, such as the dust impact spectrometers on the VEGA and Giotto missions, which analyzed the $\sim$70–80 km s^{-1} dust at comet Halley [*Dallman et al.*, 1977], are direct probes of composition [*Kissel et al.*, 1986], but such opportunities are rare.

2. Experiment

2.1. Laser Simulation of Impact Plasma

[4] Pulsed laser ablation is an accessible and flexible alternative for studying impact plasmas [*Pirri*, 1977; *Roybal et al.*, 1995]. Irradiances up to $\varepsilon \sim 10^{13}$ W cm^{-2} are readily achieved by focusing a 10–100 millijoule-class Q-switched laser (e.g., Nd:YAG) to a diameter d $\sim$ 10–10^3 μm. The few-ns pulse duration is comparable to the impact interaction time of a roughly spherical micrometeorite with a diameter of tens of μm impacting at tens of km s^{-1}. However, one must take care when interpreting the laser irradiance $\varepsilon = \Delta E/At$, with pulse energy ΔE, spot area A, and duration t, in terms of the kinematic impact irradiance $\varepsilon_{HVI} = KE/\pi r^2 t \sim \rho v^3/3$ associated with a body of density ρ and velocity v. A laser pulse couples quite differently to the target than does a solid impactor [*Kostin et al.*, 1997]: its energy is absorbed much more efficiently and over a shallower region. Furthermore, much of the laser pulse is absorbed above the surface in the expanding plume, rapidly energizing volatilized atoms. As such, crater formation, solid shock, and ejecta patterns are qualitatively different between the laser and impact cases. However, the ionizing impact vapor plume itself, during expansion, cooling, and recombination [*Hornung et al.*, 1996], may be effectively simulated with a pulsed laser at irradiances two to four

0094-8276/03/2002GL016422$05.00

orders of magnitude lower than the "equivalent" micrometeorite impact irradiance.

[5] The choice of laser parameters for our impact plasma study was based on the measurements by the PUMA instruments on the VEGA spacecraft [*Kissel et al.*, 1986], in which ~10 nm to 1 μm dust particles (mass 10^{-18} to 10^{-12} g) impacted a silver plate at ~80 km s^{-1}, producing only singly-charged plasma ions with kinetic energies (KEs) of 50–70 eV. The irradiances we used to produce the corresponding laser plasma were in the range of $\varepsilon \sim 10^9$–10^{10} W cm^{-2}, and estimates have shown that a 50 μm laser spot size generates a plasma volume comparable to that of a 10 μm dust particle impact.

[6] The reflectron TOF analyzer used was based upon a technique developed for in situ chemical analysis on planetary probes [*Brinckerhoff et al.*, 2000; *Managadze and Shutyaev*, 1993]. A Q-switched Nd:YAG laser, with infrared wavelength 1064 nm, maximum pulse energy 25 mJ, and pulse duration 6 ns, was focused through a variable attenuator to a 30–100 μm diameter spot on the target surface *in vacuo* (0.1 μTorr). In contrast to other laser mass spectrometers, ions were not extracted from the source through a large electric potential. The plume formed and expanded in zero external field, as is the case with impacts. A two-stage band-pass reflectron focused a selected KE range onto the detector. As ions formed in different ways attain distinct KE distributions, we were able to distinguish molecules that recombined from atomic ions in the plume (at higher KEs ~ 30 eV) from those desorbed intact from the target (at lower KEs ~ 1 eV). The use of real-time (shot-by-shot) TOF-MS also permitted a "direct" analysis of plasma synthesis [*Managadze*, 2001a] as opposed to an "indirect" process wherein ion signals from laser pulses are integrated over time. The latter method concentrates trace constituents but does not isolate plume-formed from surface-desorbed species.

2.2. Vapor Plume Analyses

[7] Carbon-based target materials were selected for that element's central role in complex molecular synthesis [*Kobayashi and Saito*, 2000], and given the small volume of the simulated plume. High purity carbon, with a volumetric component of hydrogen verified by a surface stripping method, and C-rich substances were used. In the mass spectra from pure carbon (Figure 1), singly-ionized, alkanes, alkenes, and other C_NH_M oligomers were identified with $N = 1$ to 40 (up to $N = 10$ shown in Figure 1) and $M = 1$ to 4. Spectra were highly reproducible, although the mass resolution was degraded at the higher masses due to reflectron defocusing in the lower kinetic energy range. C_{60} was also detected (*m*/*z* 720, Figure 1 inset, averaged signal) in some spectra at slightly higher irradiance. The C_{60} signal level was quite low, relative to the smaller masses, when compared to that seen in other studies of the *in vacuo* laser vaporization of graphite at similar irradiances [e.g., *Zhang et al.*, 1999]. We suggest that the limited cluster sizes and the low C_{60} yield observed reflect our experimental isolation of the prompt, plasma-synthesized molecular ions from the total population of evaporated species (mainly neutral molecular fragments). Vaporized neutral fragments may serve as precursors to larger clusters which are not detected here. The peaks between *m*/*z* 780 and 800 in Figure 1 (inset) were not identified. Spectra similar to Figure 1 were also obtained with polycrystalline graphite, paraffin, and bitumen targets [*Managadze*, 2001a; 2001b].

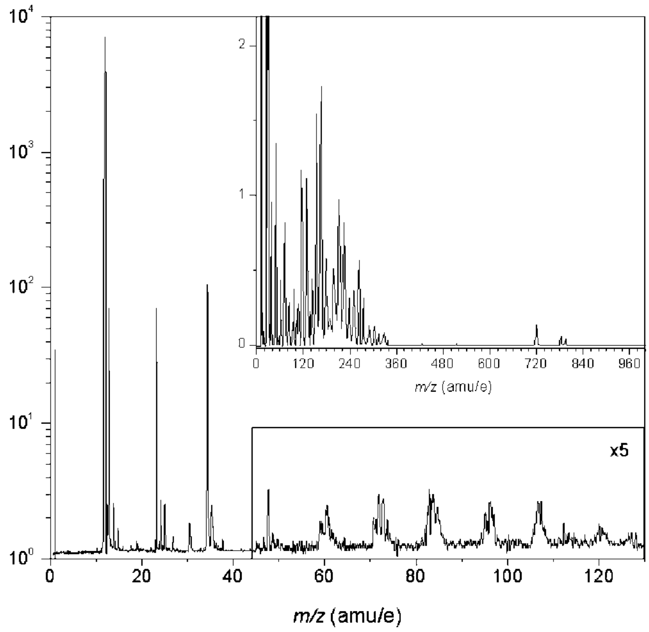

Figure 1. Laser mass spectral data for a carbon target, within the kinetic energy range 30–40 eV. The 1064 nm Nd:YAG laser irradiance was about 2 GW cm^{-2} (pulse duration 6 ns, focus diameter 50 μm). Vertical axis is arbitrary logarithmic scale. Inset: Average of mass spectra for irradiances $\geq$2 GW cm^{-2}.

[8] As the irradiance was increased from $\varepsilon \sim 1$ GW cm^{-2} toward 10 GW cm^{-2}, multiply-charged C^{2+}, C^{3+}, and C^{4+} atomic peaks emerged uniformly as expected. However, ablation of the paraffin target at $\varepsilon \sim 5$–10 GW cm^{-2} additionally produced peaks corresponding to multiply-charged hydrocarbon ions (Figure 2). Identifiable peaks were mostly limited to those with $N = 1$ or 2, but included several where the charge state exceeded M (e.g., CH_2^{3+} at *m*/*z* 4.67), indicating that such ions are not formed only by protonation of neutrals. The formation of such ions in laser induced plasmas does not appear to have been reported previously, but their appearance may be related to multiple charge exchange or stripping processes [*Andrews et al.*, 1992].

[9] A number of factors support the assertion that the observed spectra represent chemical synthesis in the plume, rather than survival (cluster desorption) of molecular fragments [cf. *Ramendik et al.*, 1979; *Bulgakov et al.*, 2000]. First, the high-density plasma produced from carbonaceous targets at these irradiances atomizes its constituents with very high efficiency [*Avrorin et al.*, 1996]. Second, the experimental configuration essentially excludes the detection of ions produced outside the plasma. Without an extraction field, ions formed from desorbed species (such as those from the lower-irradiance region around the central laser spot or from slower thermal processes) are not imparted with sufficiently high kinetic energies to be seen in the analytical window. Third, the multiply-charged hydrocarbons (e.g., CH_4^{4+}) observed above 5 GW cm^{-2} occurred simultaneously with singly-charged ions and

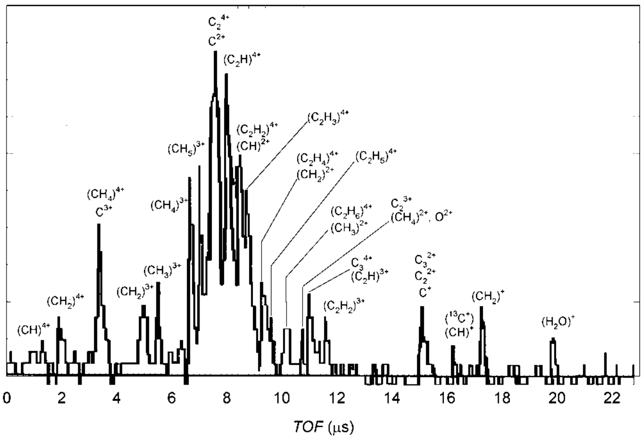

Figure 2. Laser TOF spectrum from paraffin sample, showing multiply-ionized hydrocarbon peaks. Laser irradiance was 5 GW cm^{-2}. Vertical axis is arbitrary linear scale.

increased in number as ε increased. These likely derived from an initially-atomic plume of ions and neutrals, as an intact molecule is highly unlikely to survive multiple direct plasma ionization events at these energies.

[10] Additional evidence was obtained with a physical mixture of C and Si powders (no Si-C bonds present initially) used as a target (Figure 3). In a series of such spectra we observed Si_P^+ ($P \leq 11$), $Si_PC_N^+$ and $Si_PC_NH_M^+$ (P = 1 to 7, N and M = 1 to 3) cations. The target was scanned to assure that multiple laser "impacts" were not sampling laser-fused target material, which could contain carbide species.

3. Discussion

[11] The present study is restricted to those species formed in the cooling supercritical atomic plume [*Zel'dovich and Raiser*, 1966], where the conditions in the laser and impact cases are similar. Drawing parallels beyond this case, such as at lower velocities, is more challenging. Nevertheless, organic synthesis in the plumes of sub-critical impacts at 10–15 km s^{-1} has been investigated [*Mukhin et al.*, 1989] with pulsed laser irradiation below 10^8 W cm^{-2}. The intriguing results suggested that post-impact recombination of molecular fragments also plays a synthetic role. However, in such experiments it is difficult to distinguish such species from those desorbed intact from the melt [*Chyba and Sagan*, 1992]. Very recently, dust accelerator experiments were conducted in which sub-micron carbon and latex particles impacted a pure rhodium target plate at v ≈ 16 km s^{-1}*in vacuo*. A TOF-MS similar to that of the present work detected the formation of carbon clusters up to C_{16} along with the RhC dimer, with a yield in excess of 10% [*Stübig et al.*, 2002]. We suggest that these result from plasma synthesis and provide initial confirmation of the applicability of the laser simulation.

[12] Organic/molecular ions were in fact observed with the dust impact shock mass spectrometer PUMA [*Kissel and Krüger*, 1987]. Their presence has been attributed to the protection of intact cometary organic particles by an adsorbed inorganic dust layer. We additionally suggest that plasma synthesis following the complete impact plasma atomization and ionization of some organic particles may play a role in these experiments.

[13] The yield of plasma-synthesized molecules observed in our spectra may be constrained by simple arguments without reference to an assumed model impactor. The specific energy required to form an atomic plasma ion is in the range 10–100 eV (including dissociation, ionization, and acceleration). From the integrated signals (e.g., $m/z \geq 24$ in Figure 1), and from the detector gain and instrument transmission factors [*Brinckerhoff et al.*, 2000], we estimate the yield of synthesized organics relative to ablated atoms to be at least 0.1% in the high-carbon targets. We thus infer a yield of 10^{-5} - 10^{-4} molecules eV^{-1} (10^{14}–10^{15} molecules J^{-1}). This level may be compared with prebiotic relevant to early Earth and Mars, as summarized by *Kobayashi and Saito* [2000] (based on results for glycine). The synthesis rates for hard ultraviolet radiation (~3 × 10^{17} molecules m^{-2} yr^{-1}) and cosmic rays (~6 × 10^{17} molecules m^{-2} yr^{-1}), assuming a moderately-reduced atmosphere, were much larger than that for intact delivery by meteors (~2 × 10^{15} molecules m^{-2} yr^{-1}); but at the ~10^{22} eV m^{-2} yr^{-1} estimated impact flux, our yield also gives rate of ~10^{17}–10^{18} molecules m^{-2} yr^{-1}. Although drawn from distinct sources, comparing such yields is of interest as plasma synthesis may be an enabling antecedent to radiative processes.

[14] The relative efficiency is striking for two reasons. First, the laser experiment detects only the "prompt" molecular plasma ions, which are several orders of magnitude less numerous than the neutrals. As the atomic ionization efficiency at 50–100 km s^{-1} can be very high, it is expected that the relative yield of molecular neutrals is greater than the ion yield measured here. Second, at the velocities in question, the vapor plume mass is expected to be proportional to the impactor mass and increase as the square of the velocity [*Melosh*, 1989]. It is thus possible that the path length available for plasma polymerization (or at least complexation) may have been substantial in the most

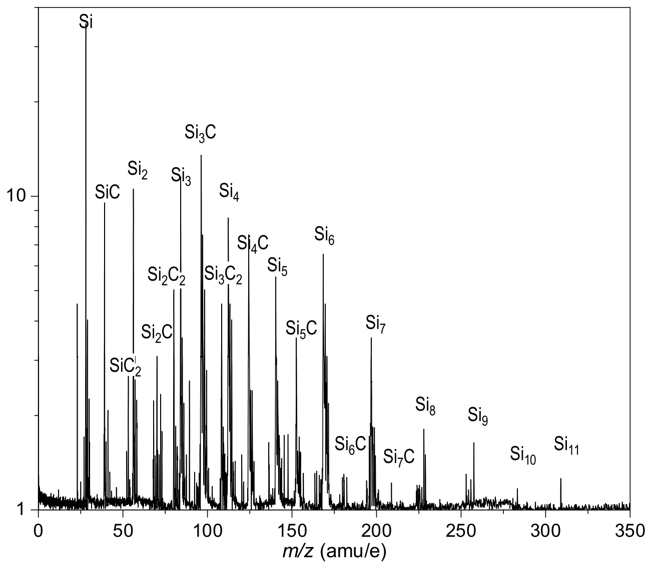

Figure 3. Laser mass spectral data from a physical mixture of C and Si powders. Vertical axis is logarithmic scale.

energetic impacts on the primitive Earth, potentially "seeding" the surface and atmosphere with precursors for processing by longer-duration mechanisms.

[15] Impacts among interstellar dust particles would not generate the large plasma volumes of meteor or small body impacts, but their "universal" prevalence may embody an altogether more substantial source of plasma-synthesized molecular precursors for chemical evolution. Over 100 interstellar molecular species have been detected in astronomical observations to date. These are synthesized from the major biogenic elements (H, C, O, and N) in cold gas phase and shock chemistry, as well as during adsorption of simple precursors on sub-micron ice-mantled dust grains. It is also possible that hypervelocity collisions among dust particles contribute significantly. Assuming a 10 nm interstellar dust particle impact velocity $v_d \sim 10^2$ km s^{-1}, our data would suggest an atomic plasma mass of $\sim 3 \cdot 10^{-17}$ g per collision, yielding $N_d \sim 10^3$ molecules of average mass 30 amu, at the observed 0.1% relative yield. Assuming the 100 km s^{-1} particles comprise only 10% of the dust population [*Spitzer*, 1978], the synthetic rate would be modulated by a collision time $\tau_d \sim [v_d(0.1\ n_d)(2\sigma_d)]^{-1} = 5 \cdot 10^{13}$ s, where $n_d \approx 10^{-8}$ cm^{-3} and $\sigma_d \approx 10^{-12}$ cm^2 are the particle concentration and cross section, respectively [*Bochkarev*, 1992]. By comparison, the adsorption of hydrogen atoms striking dust particles at $v_H \sim 1$ km s^{-1} may produce H_2 at a rate limited by $\tau'_H \sim (v_H n_d \sigma_d)^{-1} = 10^{15}$ s. In a given volume of space, the much higher hydrogen density $n_H \sim 1$ cm$^{-3} = 10^9$ (0.1 n_d) leads to a relative collision rate for H of $\sim 10^9\ \tau_d/\tau'_H = 5 \cdot 10^7$ for each such hypervelocity dust-dust impact that produces N_d molecules. H_2 formation, even if not highly efficient, must be several orders of magnitude more effective than impact synthesis of molecules. However, as the abundances of C, N, O, and S in the interstellar medium are 3–4 orders of magnitude lower than that of hydrogen, it is possible that the quantity of heavy molecules formed by plasma synthesis is not much less than that formed via surface reactions.

[16] **Acknowledgments.** The authors wish to acknowledge valuable discussions with Dr. L. Becker, Dr. M. Moore, Dr. L. Mukhin, Dr. M. Gerasimov, Dr. O. Barnouin-Jha, and Dr. L. Rudakov. The constructive reviews by Dr. S. Sugita and one anonymous reviewer are particularly appreciated. This work was partially supported by a grant from the National Aeronautics and Space Administration.

References

Andrews, S. R., et al., A combined experimental and theoretical investigation of $C_2H_2^{2+}$ electronic-state energies, *Chem. Phys.*, *166*, 69–76, 1992.

Avrorin, E. N., et al., Numerical simulation of the interaction of dust particles of a comet with a spacecraft, *Combust. Explo. Shock*, *32*, 219–224, 1996.

Bochkarev, N. G., *Foundations of the Physics of Interstellar Space*, Moscow University Press, Moscow, 1992.

Brinckerhoff, W. B., et al., Laser time-of-flight mass spectrometry for space, *Rev. Sci. Instrum.*, *71*, 536–545, 2000.

Bulgakov, A. V., et al., Laser ablation synthesis of phosphorous clusters, *Chem. Phys. Lett.*, *320*, 19–25, 2000.

Chyba, C., and C. Sagan, Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: An inventory for the origins of life, *Nature*, *355*, 125–132, 1992.

Dallman, B.-K., et al., The ion composition of the plasma produced by impacts of fast dust particles, *Planet. Space Sci.*, *25*, 135–147, 1977.

Goldsmith, D., T. Owen, *The Search for Life in the Universe*, 2nd edition, pp. 195–199, Addison-Wesley, Reading, 1992.

Hornung, K., et al., Modeling of the very high velocity impact process with respect to in situ ionization measurements, *Adv. Space Res.*, *17*, 77–86, 1996.

Kissel, J., and F. R. Krüger, The organic component in dust from comet Halley as measured by the PUMA mass spectrometer on board VEGA 1, *Nature*, *326*, 755–760, 1987.

Kissel, J., et al., Composition of comet Halley dust particles from Vega observations, *Nature*, *321*, 280–282, 1986.

Knabe, W., and F. R. Krüger, Ion formation from alkali iodide solids by swift dust particle impact, *Z. Naturforsch.*, *37A*, 1335–1340, 1982.

Kobayashi, K., and T. Saito, Energetics for chemical evolution on the primitive Earth, in *The Role of Radiation in the Origin and Evolution of the Life*, edited by M. Akaboshi et al., pp. 25–38, Kyoto Univ. Press, Kyoto, 2000.

Kostin, V. V., et al., Research on shock-wave and destruction processes at high-speed impact and laser influence on a target from an organic material, *Thermophys. High Temp.*, *35*, 962–967, 1997.

Managadze, G. G., Synthesis of organic compounds in experiments modeling high-speed meteorite impacts, IKI Preprint Pr-2037, Russian Academy of Sciences, Moscow, Russia, March, 2001a.

Managadze, G. G., Organic compound synthesis in experiments modeling highspeed meteor impact, *Geophys. Res. Abstracts*, *3*, 7595, 2001b.

Managadze, G. G., and I. Y. Shutyaev, Exotic instruments and applications of laser ionization mass spectrometry in space research, in *Laser Ionization Mass Analysis*, edited by A. Vertes et al., pp. 505–547, John Wiley, New York, 1993.

Melosh, H. J., *Impact Cratering: A Geological Process*, pp. 122–123, Oxford Univ. Press, New York, 1989.

Mukhin, L. M., et al., Origin of precursors of organic molecules during evaporation of meteorites and mafic terrestrial rocks, *Nature*, *340*, 46–48, 1989.

Pirri, A. N., Theory for laser simulation of hypervelocity impact, *Phys. Fluids*, *20*, 221–228, 1977.

Ramendik, G. I., et al., On possibility of mass-spectrometric studies of chemical processes in the plasma, *Doklady AN USSR*, *245*, 1166–1169, 1979.

Ratcliff, P. R., et al., Experimental measurements of hypervelocity impact plasma yield and energetics, *Int. J. Impact Engng.*, *20*, 663–674, 1997.

Roybal, R., et al., Laboratory simulation of hypervelocity debris, *Int. J. Impact Engng.*, *17*, 707–718, 1995.

Spitzer, L., *Physical Processes in the Interstellar Medium*, John Wiley, New York, 1978.

Stübig, M., et al., Time-of-flight mass spectra from new projectile materials for calibration of the micrometeorite detector CDA, *Geophys. Res. Abstracts*, *4*, 1364, 2002.

Thareja, R. K., et al., Interaction of ambient nitrogen gas and laser ablated carbon plume: Formation of CN, *Nucl. Instr. Meth. Phys. Res.*, *192*, 301–310, 2002.

Zel'dovich, Ya. B., and Yu. P. Raiser*Physics of Shock Waves and High Temperature Hydrodynamical Phenomena*, Nauka, Moscow, 1966.

Zhang, R., et al., Laser ablation mass spectrometry of pyrolyzed Koppers coal-tar pitch: a precursor for fullerenes and metallofullerenes, *J. Phys. Chem.*, *103*, 9450–9458, 1999.

W. B. Brinckerhoff, Applied Physics Laboratory, The Johns Hopkins University, 11100 Johns Hopkins Road, Laurel, MD 20723-6099, USA. (William.Brinckerhoff@jhuapl.edu)

G. G. Managadze and A. E. Chumikov, Space Research Institute (IKI), Moscow, Russia.